Climbing of a High Molecular Weight Liquid on a Vertical Solid Surface Grafted with Long Polymer Chains

Miguel Aubouy,[†] **Françoise Brochard-Wyart,**[‡] **and Elie Raphaël***,[†]

Laboratoire de Physique de la Matière Condensée, URA 792 CNRS, Collège de France, 11 Place Marcelin-Berthelot, 75231 Paris Cedex 05, France, and P.S.I. Institut Curie, 11 rue Pierre et Marie Curie, 75231 Paris Cedex 05, France

ABSTRACT: We discuss the climbing of a high molecular weight liquid (P monomers per chain) on a vertical solid surface grafted with long polymer tails (N monomers per chain). We assume the liquid and the grafted tails to be chemically identical. Using a Flory-type approach, we calculate the thickness L of the film as a function of the reduced altitude $\bar{h} = h/h_c$, the degrees of polymerization P and N, and the grafting density σ. The characteristic height h_c is defined by $h_c = kT/(\rho g a^3)$, where ρ is the liquid density and a a molecular size. Several regimes are found. In the particular case where at $h = 0$ the grafted tails are stretched and some mobile chains are still present in the brush, we predict that (a) at small altitude ($\bar{h} < P^{-1/3}\sigma^{4/3}$), gravity is a small perturbation and $L \simeq aNP^{-1/3}\sigma^{1/3}(1 - \bar{h}P^{1/3}\sigma^{-4/3})$ and (b) at higher altitude, gravitational effects are important and $L \simeq aNP^{-1/3}\sigma^{1/3}(\bar{h}P^{1/3}\sigma^{-4/3})^{-1/2}$.

1. Introduction

At high enough coverage, polymer chains tethered by one end to a flat solid surface stretch away forming a polymer "brush". In the past 15 years polymer brushes have been the subject of numerous theoretical and experimental studies. The scaling arguments of Alexander and de Gennes[1,2] have recently been followed by computer simulations[3,4] and self-consistent field calculations.[5–8] Recent reviews on polymer brushes can be found in refs 9 and 10.

Consider polymer chains with degree of polymerization N terminaly grafted onto a flat surface and exposed to a solvent made of chemically identical chains with degree of polymerization P.[2,11,12] The number of terminally grafted chains per unit area is σa^{-2}, where a is the monomer size. The average distance between two grafting sites is given by $D = a\sigma^{-1/2}$. At sufficiently low σ, the grafted polymers do not overlap (the so-called "mushroom" regime[2]). In this regime, the thickness L_0 of the layer is given by $L_{0(1)} \simeq aN^{1/2}$ for $P > N^{1/2}$ and $L_{0(2)} \simeq aN^{3/5}P^{-1/5}$ for $P < N^{1/2}$ (regions 1 and 2 of the (P,σ) diagram represented in Figure 1). As σ increases, the grafted chains begin to overlap for $D \simeq L$. This defines an overlap concentration: $\sigma_{ov} \simeq P^{2/5}N^{-6/5}$ for $P < N^{1/2}$ and $\sigma_{ov} \simeq N^{-1}$ for $P > N^{1/2}$. In a simple Flory picture, the free energy per chain for $\sigma > \sigma_{ov}$ is given by

$$\frac{F}{kT} \simeq \frac{L^2}{a^2N} + \frac{a^3}{P}\frac{N^2}{LD^2} \tag{1.1}$$

The first term in eq 1.1 represents the elastic contribution. The second term corresponds to the effect of two-body interactions; the factor P^{-1} corresponds to the Edwards screening of the excluded volume interactions.[13] Minimizing the free energy (1.1), we get $L_{0(3)} \simeq aNP^{-1/3}\sigma^{1/3}$. This corresponds to region 3 of the (P,σ) diagram. In what follows we will call this regime the "stretched regime".

Note that in eq 1.1 we have omitted the expanding contribution a^2NL^{-2}. This omission is legitimate as long
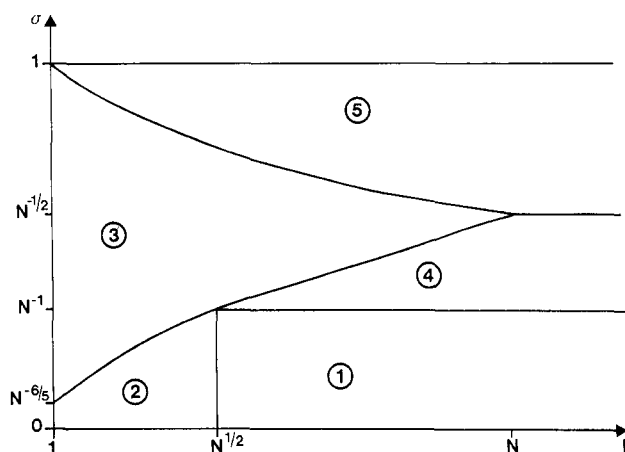
† Collège de France.
‡ P.S.I. Institut Curie.

Figure 1. Schematic (P,σ) diagram of a polymer brush exposed to a chemically identical high molecular weight solvent. The thickness of the brush in the different regions is given by (1) $L \simeq aN^{1/2}$, (2) $L \simeq aN^{3/5}P^{-1/5}$, (3) $L \simeq aNP^{-1/3}\sigma^{1/3}$, (4) $L \simeq aN^{1/2}$, and (6) $L \simeq aN\sigma$. The crossovers between the different regions are given in Appendix 2.

as the ratio

$$\xi = \frac{a^2N}{L_{0(3)}^2}\left(\frac{a^3}{P}\frac{N^2}{L_{0(3)}D^2}\right)^{-1} \simeq \sigma^{-1}PN^{-3/2} \tag{1.2}$$

is smaller than unity. For $\sigma < PN^{-3/2}$, the perturbation parameter ξ is greater than unity and the Flory free energy is given by

$$\frac{F}{kT} \simeq \frac{L^2}{a^2N} + \frac{a^2N}{L^2} \tag{1.3}$$

which leads to $L_{0(4)} \simeq aN^{1/2}$. The regime $\sigma < PN^{-3/2}$ corresponds to region 4 of the (P,σ) diagram. We will refer to this regime as the "screened regime".

Starting from region 3 or 4 and increasing σ, we reach region 5 where the mobile chains are almost completely expelled from the brush: the brush is "dry". In this region, the volume fraction of the grafted polymer is of order unity, and the brush thickness is given by $L_{0(5)} \simeq aN\sigma$. The crossovers between the different regions of the (P,σ) diagram are given in Appendix 2.

Consider now the less familiar case represented in Figure 2: the grafted surface (N monomers per chain) is vertical

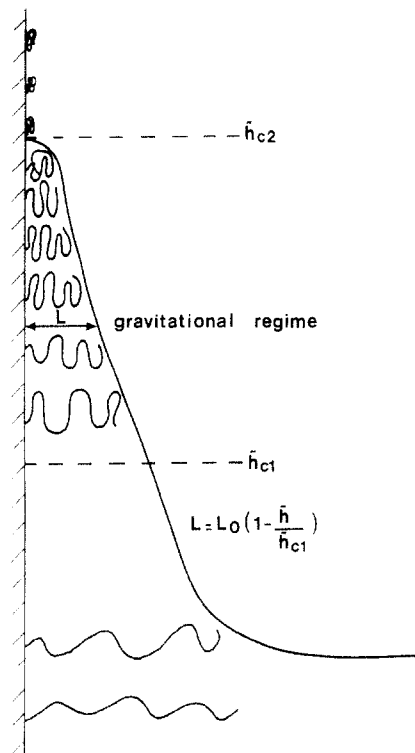**Figure 2.** Climbing of a high molecular weight liquid on a vertical plate grafted with long polymer chains. For $\tilde{h} < \tilde{h}_{c1}$ gravity can be treated as a small perturbation. For $\tilde{h} > \tilde{h}_{c1}$ gravitational effects are important. The film stops at an altitude $\tilde{h}_{c2}$.

and in contact with a high molecular weight (degree of polymerization P), chemically identical solvent. To reduce the layer free energy the liquid climbs and impregnates the grafted chains. Since this process is limited by gravity, the thickness of the brush decreases with the altitude h. In this paper, we primarily study the variations of the equilibrium thickness L with h. This generalizes the recent work of Brochard-Wyart and de Gennes,[14] who considered the case of a low molecular weight solvent ($P = 1$). We assume that the solvent partially wets the solid surface: in the absence of grafted tails the solvent would reach an altitude $H = 2\kappa^{-1} \sin(\pi/4 - \theta/2)$, where θ is the Young's contact angle and κ^{-1} the capillary length (defined by $\kappa^{-2} = \gamma/\rho g$, where ρ is the solvent density and γ the solvent/ air surface tension).[15] In what follows we will focus on altitudes larger than H so that the meniscus plays no role. We also assume that the grafted tails do not adsorb at the solid–liquid interface. At reservoir level (i.e., for $h = 0$), the equilibrium thickness of the brush is not affected by gravity and we recover the results discussed previously. At finite altitude h, the osmotic pressure inside the brush must increase to balance the gravitational energy (per unit volume) of the solvent, and therefore the brush thickness decreases. We can define a reduced altitude $\tilde{h}$ by $\tilde{h} = \Delta\mu/(kT) = h/h_c$, where $\Delta\mu = \rho g h a^3$ is the gravitational energy per solvent monomer and a a molecular size; the characteristic height is defined by $h_c = kT/(\rho g a^3)$ ($h_c = 1$ km for $\rho = 1$ g·cm^{-3} and $a = 1$ nm).

The organization of the paper is as follows. We first calculate (section 2) the thickness of the brush L as a function of reduced altitude $\tilde{h}$ in the case where at $\tilde{h} = 0$ the brush is in region 3 of the (P,σ) diagram (case of an initially "stretched brush"). We then investigate (section 3) the case of an initially "screened brush" (region 4 of the (P,σ) diagram). We use simple Flory arguments to derive the thickness of the brush, and we will neglect all numerical coefficients in the equations. The main results are also compared to those derived from self-consistent field

arguments. In Appendix 1 we discuss the particular case where at $\tilde{h} = 0$ the grafted layer is in the mushroom regime.

2. Climbing on a Grafted Polymer Brush: Case of a Stretched Brush

We consider a brush which for $\tilde{h} = 0$ is in region 3 of the (P,σ) diagram. At an altitude $\tilde{h}$ above the reservoir the Flory free energy per chain is given by

$$\frac{F}{kT} \cong \frac{L^2}{a^2 N} + \frac{a^3}{P}\frac{N^2}{LD^2} + \tilde{h}\frac{LD^2}{a^3} \qquad (2.1)$$

where the third term on the right-hand side corresponds to the gravitational energy of the solvent. The minimization of eq 2.1 leads to a balance between osmotic, elastic, and hydrostatic contributions:

$$\frac{L}{a^2 N} - \frac{a^3}{P}\frac{N^2}{L^2 D^2} + \tilde{h}\frac{D^2}{a^3} = 0 \qquad (2.2)$$

(a) At small altitude, the hydrostatic contribution can be treated as a perturbation and eq 2.2 leads to

$$L \cong aNP^{-1/3}\sigma^{1/3}\left(1 - \frac{\tilde{h}}{P^{-1/3}\sigma^{4/3}}\right) =$$
$$L_{0(3)}\left(1 - \frac{\tilde{h}}{P^{-1/3}\sigma^{4/3}}\right) \qquad (2.3)$$

(b) At higher altitude the elastic term becomes negligible. The balance between the osmotic and the hydrostatic terms leads to

$$L \cong L_{0(3)}\left(\frac{\tilde{h}}{P^{-1/3}\sigma^{4/3}}\right)^{-1/2} \qquad (2.4)$$

The crossover between regimes a and b occurs for $\tilde{h} \cong \tilde{h}_{c1}$, with

$$\tilde{h}_{c1} \cong \sigma^{4/3}P^{-1/3} \qquad (2.5)$$

(c) At even higher altitude ($\tilde{h} > \tilde{h}_{dry}$), the brush becomes "dry"; i.e., the volume fraction of the grafted chains becomes of order unity. In this region the brush thickness is given by $L \cong aN\sigma$. The altitude $\tilde{h}_{dry}$ is given by setting $L = aN\sigma$ in eq 2.4:

$$\tilde{h}_{dry} \cong P^{-1} \qquad (2.6)$$

We end this section with some remarks:

(i) Equation 2.1 assumes that two-body interactions dominate over the expanding contribution $a^2 NL^{-2}$. To check if this assumption is valid, we define a perturbation parameter ξ' as

$$\xi' = \left(\frac{a^3}{P}\frac{N^2}{LD^2}\right)^{-1}\frac{a^2 N}{L^2} \cong \left(\frac{\tilde{h}}{\sigma^4 N^4 P^{-3}}\right)^{1/3} = \left(\frac{\tilde{h}}{\tilde{h}_{c3}}\right)^{1/3} \qquad (2.7)$$

If $\tilde{h}_{c3}$ is larger than $\tilde{h}_{dry}$ (eq 2.6), the previous calculations (eqs 2.1–2.6) remain unchanged. Assume $\tilde{h}_{c3} < \tilde{h}_{dry} \cong P^{-1}$. For $\tilde{h} < \tilde{h}_{c3}$, ξ' is smaller than unity, and the brush thickness is given by eqs 2.3 and 2.4. For $\tilde{h} > \tilde{h}_{c3}$, the expanding contribution $a^2 NL^{-2}$ dominates over two-body interactions, and the Flory free energy per chain can be written as

$$\frac{F}{kT} \cong \frac{L^2}{a^2 N} + \frac{a^2 N}{L^2} + \tilde{h}\frac{LD^2}{a^3} \qquad (2.8)$$

The minimization of eq 2.8 leads to

$$\frac{L}{a^2 N} - \frac{a^2 N}{L^3} + \tilde{h}\frac{D^2}{a^3} = 0 \qquad (2.9)$$

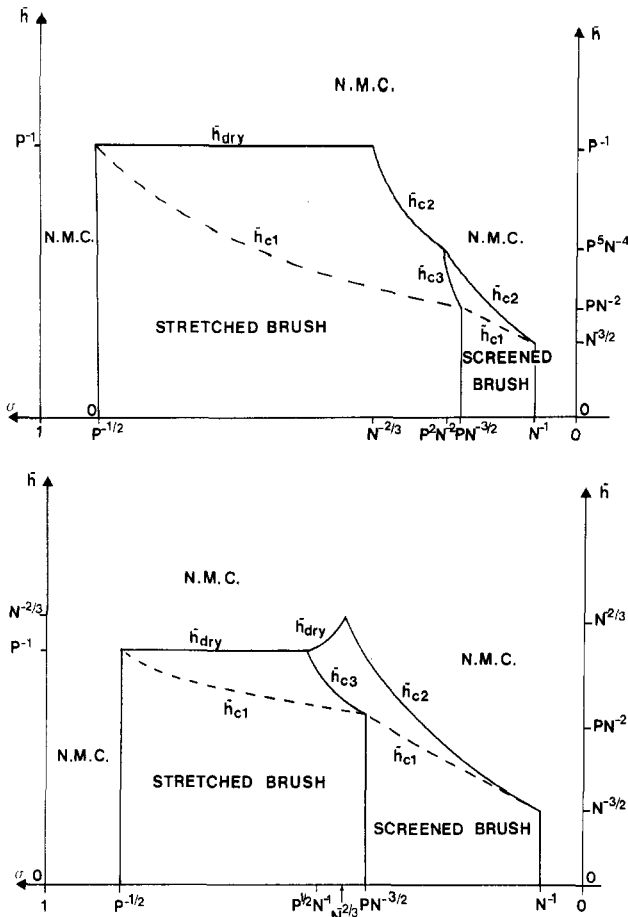If we assume that for $\tilde{h} > \tilde{h}_{c3}$ the elastic contribution eq

Figure 3. Schematic representation of the evolution of $\bar{h}_{dry}$, $\bar{h}_{c2}$, and $\bar{h}_{c3}$ (the crossover between the stretched and the screened regimes) with σ and P. The dashed lines represent the evolution of $\bar{h}_{c1}$. The symbol N.M.C. stands for no mobile chains. The crossovers between the different regions are given in Appendix 3. Top: $N^{1/2} < P < N^{2/3}$. Bottom: $P > N^{2/3}$.

2.9 is negligible compared to the gravitational term, the brush thickness is given by

$$L \simeq aN^{1/2}\left(\frac{\bar{h}}{N^{-1/2}\sigma}\right)^{-1/3} \tag{2.10}$$

The reduced altitude $\bar{h}_{dry}$ above which the brush is dry is now given by

$$\bar{h}_{dry} \simeq N^{-2}\sigma^{-2} \tag{2.11}$$

(ii) The climbing process might be described by the following scenario. Suppose the climbing liquid has just reached an altitude h. The collapsed tail at altitude h is then in contact with the liquid and starts to swell. While swelling, its spatial extension grows and we expect it to be comparable with L. If $L > D$, the next collapsed tail (which is at an altitude $h + D$) is then reached by the liquid. At high altitude the thinning is important and we may find $L < D$. The previous picture would not be valid anymore and we expect the film to stop rising (remember that, by assumption, the mobile chains wet *partially* the bare surface). This would occur for a reduced altitude $\bar{h}_{c2}$ where L is of order D. In Appendix 3 we give the maximum altitude $\bar{h}_{max}$ reached by the liquid. This altitude corresponds to the minimum of $\bar{h}_{dry}$ and $\bar{h}_{c2}$. See also Figure 3.

(iii) The brush picture adopted in this paper (steplike concentration profile and all free ends at the same distance from the surface) imposes strong constraints on the allowed chain configurations. Some time ago Milner *et al.*[6,7] and Zhulina *et al.*[8] solved analytically the self-consistent field

(SCF) equations for the brush but relaxing the above-mentioned restrictions. They found that the brush volume fraction $\phi(z)$ at a distance z from the solid surface was essentially parabolic. In the case of a high molecular weight solvent with degree of polymerization P, one gets[8]

$$\phi(z) = \frac{\pi^2 P}{8a^2 N^2}(L_0^2 - z^2) \tag{2.12}$$

In eq 2.12 L_0 is the natural extension of the brush:

$$L_0 = (12\pi^{-2})^{1/3}P^{-1/3}\sigma^{1/3}Na \tag{2.13}$$

For a brush under compression, the thickness L of the brush is smaller than L_0. The brush volume fraction is then a truncated parabola:[6,7]

$$\phi(z) = \frac{\pi^2 P}{8a^2 N^2}(L'_0{}^2 - z^2)\,\theta(L-z) \tag{2.14}$$

where $\theta(L-z) = 1$ if $L > z$ and 0 otherwise. The length L'_0 (which is larger than L_0) can be determined from the conservation of the total number of monomers.

Let us now consider the case of a vertical grafted surface: at a given altitude h, the brush is under compression due to the hydrostatic pressure. At the outer extremity of the brush, the osmotic pressure balances the hydrostatic pressure (since the grafted tail ends are free, the elastic contribution vanishes):

$$\tfrac{1}{2}P^{-1}\phi^2(z=L) = \bar{h} \tag{2.15}$$

Combining eqs 2.14 and 2.15, we obtain

$$L'_0 = \left(L^2 + \frac{8a^2 N^2}{\pi^2 P}(2P\bar{h})^{1/2}\right)^{1/2} \tag{2.16}$$

The conservation of the total number of monomers imposes: $\int_0^L \phi(z)\,dz = aN\sigma$. Using eqs 2.14 and 2.16, we get

$$L^3 + 12\pi^{-2}(2P^{-1}\bar{h})^{1/2}N^2 a^2 L \simeq 12\pi^{-2}\sigma P^{-1}N^3 a^3 \tag{2.17}$$

As in the case of the Flory approach, two regions are found:

At small altitude ($\bar{h} < \bar{h}_{c1}$, where now $\bar{h}_{c1} \simeq \tfrac{1}{2}(12\pi^{-2})^{-2/3}\sigma^{4/3}P^{-1/3}$) gravity can be treated as a perturbation and

$$L \simeq (12\pi^{-2})^{1/3}P^{-1/3}\sigma^{1/3}Na\left\{1 - \frac{1}{3}\left(\frac{\bar{h}}{2^{-1}(12\pi^{-2})^{-2/3}\sigma^{4/3}P^{-1/3}}\right)^{1/2}\right\} \tag{2.18}$$

At higher altitude ($\bar{h} > \bar{h}_{c1}$) the osmotic pressure balances the hydrostatic pressure:

$$L \simeq (12\pi^{-2})^{1/3}P^{-1/3}\sigma^{1/3}Na\left(\frac{\bar{h}}{2^{-1}(12\pi^{-2})^{-2/3}\sigma^{4/3}P^{-1/3}}\right)^{-1/2} \tag{2.19}$$

The SCF predictions for the crossover altitude $\bar{h}_{c1}$ and for the brush thickness L in the regime $\bar{h} > \bar{h}_{c1}$ are identical to the Flory-type predictions (up to numerical coefficients). However, at small altitude ($\bar{h} < \bar{h}_{c1}$), the SCF calculation predicts a more important thinning of the brush: $\Delta L \sim \bar{h}^{1/2}$, whereas $\Delta L \sim \bar{h}$ in the Flory picture. This difference might be traced back to the inner structure of the brush: in the SCF picture, the concentration profile (and hence the osmotic pressure) vanishes continuously at the outer extremity of the brush, leading to a larger deformation under small compression.

3. Climbing on a Grafted Polymer Brush: Case of a Screened Brush

We now consider the climbing of the high molecular weight solvent onto a grafted polymer layer which at $h = 0$ is in region 4 of the (P,σ) diagram (case of an initially screened brush). As discussed in the Introduction, excluded volume effects are negligible in region 4, and the Flory free energy per chain is given by (1.3). At finite altitude the Flory free energy per chain becomes

$$\frac{F}{kT} \cong \frac{L^2}{a^2 N} + \frac{a^2 N}{L^2} + \tilde{h}\frac{LD^2}{a^3} \qquad (3.1)$$

(a) At small altitude, the third term on the right-hand side can be treated as a perturbation and

$$L \cong aN^{1/2}\left(1 - \frac{\tilde{h}}{N^{-1/2}\sigma}\right) = L_{0(4)}\left(1 - \frac{\tilde{h}}{N^{-1/2}\sigma}\right) \quad (3.2)$$

(b) At higher altitude ($\tilde{h} > \tilde{h}_{c1}$) the elastic term becomes negligible and $L \cong L_{0(4)}(\tilde{h}N^{1/2}\sigma^{-1})^{-1/3}$. The crossover altitude $\tilde{h}_{c1}$ between regimes a and b is obtained by equating the elastic and the gravitational terms in eq 2.9. This leads to

$$\tilde{h}_{c1} \cong N^{-1/2}\sigma \qquad (3.3)$$

(c) At even higher altitude, $\tilde{h} > \tilde{h}_{dry} \cong N^{-2}\sigma^{-2}$, the brush becomes dry. Note that if the brush thickness L becomes smaller than D, we expect the climbing to stop. This is discussed in Appendix 1.

4. Concluding Remarks

Surfaces grafted with polymers have been the subject of numerous theoretical and experimental works but less is known about their behavior in the presence of a high molecular weight solvent.[16] The climbing of a high molecular weight liquid on a vertical grafted solid surface may provide an interesting experimental tool to study these systems. It may also provide an experimental method to check the predictions of the self-consistent field calculations.

The variations of the brush thickness with altitude can be measured by light reflectivity. Preliminary observations by Deruelle and Léger[17] on vertical brushes of PDMS ($N \cong 4000$) in contact with toluene are promising.

Appendix 1

In this appendix we consider the case where at $h = 0$, the grafted layer (GL) is in the mushroom regime (region 1 or 2 of the (P,σ) diagram). Since $D > L$, we do not expect the film to climb. Let us however consider another situation where the GL is first *totally* immersed in the solvent reservoir and then *partially* pulled out. At equilibrium we expect each grafted chain to form a hemisphere of radius $R = R(\tilde{h})$ containing some mobile chains (see Figure 4).

1. If at $h = 0$ the GL is in region 2 of the (P,σ) diagram, the Flory free energy per chain at finite altitude is given by

$$\frac{F}{kT} \cong \frac{R^2}{a^2 N} + \frac{a^3}{P}\frac{N^2}{R^3} + \tilde{h}\frac{R^3}{a^3} \qquad (A.1)$$

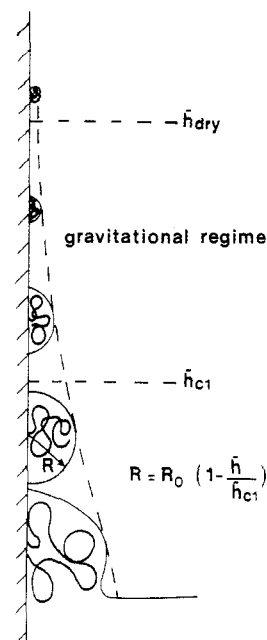From eq A.1 one can easily calculate the radius of the

Figure 4. Variations of the mushroom radius in the case of a brush initially immersed in a solvent reservoir and then partially pulled out. For $\tilde{h} < \tilde{h}_{c1}$ gravity can be treated as a small perturbation. For $\tilde{h} > \tilde{h}_{c1}$ gravitational effects are important. No mobile chains can be found above the reduced altitude $\tilde{h}_{dry}$.

mushrooms:

$$R \cong aN^{3/5}P^{-1/5}\left(1 - \frac{\tilde{h}}{P^{1/5}N^{-8/5}}\right) =$$

$$R_{0(2)}\left(1 - \frac{\tilde{h}}{P^{1/5}N^{-8/5}}\right) \quad \text{if } \tilde{h} < P^{1/5}N^{-8/5} \quad (A.2)$$

$$R \cong R_{0(2)}\left(\frac{\tilde{h}}{P^{1/5}N^{-8/5}}\right)^{-1/6} \quad \text{if } \tilde{h} > P^{1/5}N^{-8/5} \quad (A.3)$$

The grafted layer becomes dry when R (eq A.3) becomes of the order of $aN^{1/3}$, i.e., at an altitude

$$\tilde{h}_{dry} \cong P^{-1} \qquad (A.4)$$

2. Suppose now that at $h = 0$ the GL is in region 1 of the (P,σ) diagram. The Flory free energy per chain at finite altitude is

$$\frac{F}{kT} \cong \frac{R^2}{a^2 N} + \frac{a^2 N}{R^2} + \tilde{h}\frac{R^3}{a^3} \qquad (A.5)$$

Minimizing eq A.5, we get

$$R \cong aN^{1/2}\left(1 - \frac{\tilde{h}}{N^{-3/2}}\right) = R_{0(1)}\left(1 - \frac{\tilde{h}}{N^{-3/2}}\right)$$
$$\text{for } \tilde{h} < N^{-3/2} \quad (A.6)$$

$$R \cong R_{0(1)}\left(\frac{\tilde{h}}{N^{-3/2}}\right)^{-1/5} \quad \text{for } \tilde{h} > N^{-3/2} \qquad (A.7)$$

The grafted layer becomes dry when R (eq A.7) becomes of the order of $aN^{1/3}$, i.e., at an altitude

$$\tilde{h}_{dry} \cong N^{-2/3} \qquad (A.8)$$

In writing eq A.5, we have implicitly assumed that two-body interactions were negligible. One can show that this assumption is legitimate if $P > N^{2/3}$. For $P < N^{2/3}$, a new region $P^5N^{-4} < \tilde{h} < P^{-1}$ arises. In this region the radius R is given by $R \cong aN^{3/5}P^{-1/5}(\tilde{h}P^{-1/5}N^{8/5})^{-1/6}$. For $\tilde{h} > P^{-1}$, the grafted layer is dry.

Appendix 2

We give here the crossovers between the different regions of the (P,σ) diagram represented in Figure 1:

$$\text{region 1/region 2: } P_{co} \equiv N^{1/2}$$

$$\text{region 2/region 3: } \sigma_{co} \equiv P^{2/5}N^{-6/5}$$

$$\text{region 1/region 4: } \sigma_{co} \equiv N^{-1}$$

$$\text{region 3/region 4: } \sigma_{co} \equiv PN^{-3/2}$$

$$\text{region 3/region 6: } \sigma_{co} \equiv P^{-1/2}$$

$$\text{region 4/region 6: } \sigma_{co} \equiv N^{-1/2}$$

Appendix 3

In this appendix we give the maximum altitude $\bar{h}_{max}$ reached by the solvent ($\bar{h}_{max}$ is represented in Figure 3). This altitude corresponds to the minimum of $\bar{h}_{dry}$ and $\bar{h}_{c2}$.

When $P < N^{1/2}$

$$\bar{h}_{max} = \bar{h}_{dry} \simeq P^{-1} \quad \text{if } P^{-1/2} < \sigma < N^{-2/3}$$

$$\bar{h}_{max} = \bar{h}_{c2} \simeq \sigma^3 N^2 P^{-1} \quad \text{if } N^{-2/3} < \sigma < P^{2/5}N^{-6/5}$$

When $N^{1/2} < P < N^{2/3}$

$$\bar{h}_{max} = \bar{h}_{dry} \simeq P^{-1} \quad \text{if } P^{-1/2} < \sigma < N^{-2/3}$$

$$\bar{h}_{max} = \bar{h}_{c2} \simeq \sigma^3 N^2 P^{-1} \quad \text{if } N^{-2/3} < \sigma < P^2 N^{-2}$$

$$\bar{h}_{max} = \bar{h}_{c2} \simeq \sigma^{5/2} N \quad \text{if } P^2 N^{-2} < \sigma < N^{-1}$$

When $P > N^{2/3}$

$$\bar{h}_{max} = \bar{h}_{dry} \simeq P^{-1} \quad \text{if } P^{-1/2} < \sigma < P^{1/2}N^{-1}$$

$$\bar{h}_{max} = \bar{h}_{dry} \simeq \sigma^{-2}N^{-2} \quad \text{if } P^{1/2}N^{-1} < \sigma < N^{-2/3}$$

$$\bar{h}_{max} = \bar{h}_{c2} \simeq \sigma^{5/2} N \quad \text{if } N^{-2/3} < \sigma < N^{-1}$$

References and Notes

(1) Alexander, S. *J. Phys. (Paris)* 1977, *38*, 977.
(2) de Gennes, P.-G. *J. Phys. (Paris)* 1976, *37*, 1443; *Macromolecules* 1980, *13*, 1069.
(3) Murat, M.; Grest, G. S. *Phys. Rev. Lett.* 1989, *63*, 1074; *Macromolecules* 1989, *22*, 4054; *Macromolecules* 1991, *24*, 704.
(4) Lai, P.-Y.; Binder, K. *J. Chem. Phys.* 1991, *95*, 9299.
(5) Hirz, S. J. Modeling of Interactions Between Adsorbed Block Copolymers. M.S. Thesis, University of Minnesota, Minneapolis, MN, 1988.
(6) Milner, S. T.; Witten, T. A.; Cates, M. E. *Europhys. Lett.* 1988, *5*, 413.
(7) Milner, S. T.; Witten, T. A.; Cates, M. E. *Macromolecules* 1988, *21*, 2610.
(8) Zhulina, E. B.; Pryamitsyn, V. A.; Borisov, O. V. *Vysokomol. Soedin., Ser. A* 1989, *31*, 185. Zhulina, E. B.; Borisov, O. V. *J. Colloid Interface Sci.* 1991, *144*, 507.
(9) Milner, S. T. *Science* 1991, *251*, 905.
(10) Halperin, A.; Tirrel, M.; Lodge, T. P. *Adv. Polym. Sci.* 1991, *100*, 31.
(11) Leibler, L. *Makromol. Chem., Macromol. Symp.* 1988, *16*, 1.
(12) Raphaël, E.; Pincus, P.; Fredrickson, G. H. *Macromolecules* 1993, *26*, 1996. See also: Aubouy, M.; Raphaël, E. *J. Phys. II Fr.* 1993, *3*, 443.
(13) See, e.g.: de Gennes P.-G. *Scaling Concepts in Polymer Physics*; Cornell University Press: Ithaca, NY, 1979.
(14) de Gennes, P.-G.; Brochard-Wyart, F. *J. Adhes. Sci. Technol.* 1993, *7*, 495.
(15) See, for example: Adamson, A. W. *Physical Chemistry of Surfaces*, 5th ed.; Wiley-Interscience: New York, 1990.
(16) Zhao, X.; Zhao, W.; Rafailovich, M. H.; Sokolov, J.; Russell, T. P.; Zhao, X.; Kumar, S. K.; Schwarz, S. A.; Wilkens, B. J. *Europhys. Lett.* 1991, *15*, 725. See also: Budkowski, A.; Steiner, U.; Klein, J.; Fetters, L. *J. Europhys. Lett.* 1992, *20*, 499.
(17) Deruelle, M.; Léger, L., private communication.